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Adsorption of atmospheric oxidants at divacancy sites of graphene: A DFT study

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ABSTRACT

Periodic DFT calculations are performed to compare the reactivity with respect to atmospheric oxidants like O_2, H_2O, O_3 and atomic oxygen of different divacancy structures created in graphene sheet by removing two adjacent carbon atoms. The present approach shows that O and O_3 can easily be chemisorbed at the divacancy sites, the reaction product being however strongly dependent on the divacancy structure. The situation appears more intricate when considering the interaction of O_2 and H_2O with the defective graphene sheet. In this case, dissociative chemisorption on the surface is evidenced only when dangling bonds are present at the divacancy site.

1. Introduction

Whereas the outstanding properties of perfect graphene have now been confirmed in many studies [1], the question remains open about the effect of structural defects occurring in graphene during growth or processing [2]. On the one hand, defects can strongly deteriorate the performance of graphene-based devices but, on the other hand, they can also be useful in some applications by making possible to tailor some local properties and to achieve new functionalities [2]. Structural defects in graphene include both point defects, like Thrower–Stone–Wales defect, missing atoms (i.e., vacancies), adatoms or substitutional impurities, and extended defects like dislocations or edges [see Ref. [2] and references herein]. Although some of these defects are quite well characterized, especially edges that are known to be very reactive sites [3–7], some open questions remain concerning vacancies that are yet of great interest because they should enhance the reactivity of the basal plane of graphene, depending on the presence or absence of dangling bonds as suggested by recent calculations [8–13]. Single vacancies in graphene have been well-characterized experimentally by microscopy [14,15]. Removing one carbon atom from the surface results in the formation of two five-membered and nine-membered rings thus leaving one bond unsaturated that can make this defect very reactive [16–18]. Moreover, single vacancies can migrate on the graphene surface above room temperature and coalesce to form larger vacancies that can also be directly formed by removing several neighboring atoms [2]. Calculations indicate that double vacancies are thermodynamically favored over single vacancies [8,19,20] and, more generally, that vacancies with even number of missing atoms are more stable than those with odd number of missing atoms (at least up to 8 missing carbon atoms, the maximum number considered in calculations) [8,9,13]. The optimized structures of even vacancies are characterized by the saturation of all dangling bonds [8,9] and their reactivity is thus suspected to be quite low, in contrast with the reactivity of vacancies created by removing an odd number of carbon atoms. This has been confirmed by recent Born–Oppenheimer Molecular Dynamics simulations that have evidenced large energy barriers preventing chemisorption of O_2 and H_2O on even vacancy defects [13]. However, some theoretical studies based on energy optimization have shown that the chemisorption of O_2 on di- and four-atom vacancies is a strongly exothermic process [11,21]. A more detailed investigation on this point appears thus mandatory before definite conclusions can be drawn on the chemical reactivity of divacancies in graphene.

Moreover, this information would be useful not only for graphene science but it will also enhance our knowledge on other carbonaceous surface behavior. For instance, combustion-derived solid particles that are primarily made of carbon atoms are suspected to have a non-negligible impact on the Earth's radiative balance by accounting for both direct heating due to light absorption and

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indirect cooling because of their activation as ice and cloud condensation nuclei [22]. These particles are currently one of the largest sources of uncertainties in understanding the fossil fuel burning impact on climate, mostly due to the high natural variability of combustion particle properties in respect to their sources, conditions of combustion and fuel composition [23]. Widely accepted structural models for combustion carbonaceous particles assume the presence of graphene sheets, whose stacking on concentric spheres of different radii results in typical onion-like structures containing also other elements (mainly oxygen) besides carbon due to partial oxidation [24]. The graphene sheets constituting these complex structures are also characterized by the presence of defects, like edges or carbon atom vacancies formed during the recombination of soot precursors [25] that exhibit more or less hydrophilic behavior. Furthermore, characterizing both the structure of vacancies in graphene and their ability to promote chemical reactions, especially with atmospheric oxidants, is a mandatory preliminary step toward a better understanding of the impact of the particles emitted by engines on atmospheric chemistry and climate evolutions.

We thus extend here our previous studies on the reactivity of graphene surfaces [12,13,18] by focusing on the oxidation of the divacancies. In our approach, these divacancies are created by removing two nearest-neighbor carbon atoms in a two-dimensional infinite graphene sheet and their structure is optimized by quantum calculations. Then, the oxidation of the most stable divacancy structures is investigated by Born–Oppenheimer Molecular calculations to compare their reactivity with respect to some of the most frequent oxidizing species in the Troposphere, namely O, O_2, O_3, and H_2O. The details of the computational methods used here are briefly given in Section 2. The optimized structures for the divacancies and the results of the oxidation reactions are presented in Section 3. Finally, the main conclusions of the present study are given in Section 4.

2. Computational details

As in our previous paper [13], the defective graphene surface is modeled by a large supercell of rhombohedral shape with two-dimensional periodic conditions to represent an infinite graphene sheet. One divacancy is then created at the center of the supercell by removing two nearest neighbor C atoms. First-principle calculations based on the Density Functional Theory (DFT) are thus performed to optimize the most stable geometries of the divacancy by relaxing all degrees of freedom. Note that we consider here supercell periodic replication instead of large carbonaceous clusters to represent the graphene surface, because it has been previously shown that creating vacancies in such clusters may lead to strong out-of-plane deformation of the surface whose geometry thus strongly depends on the cluster size [12,13]. Moreover, this deformation is at odds with experimental results that have shown that graphene surface remains flat even when large vacancies are created [26].

When using periodic conditions, it is mandatory to consider a quite large number of C atoms in the rhombohedric supercell that is periodically reproduced. Indeed, not only small out-of-plane deformation might otherwise be observed but the results of the calculations themselves might be also not well converged because they depend on the size of the supercell, as shown in our previous work [13]. As a consequence, we consider here a supercell containing 162 C atoms (before the vacancy has been created) which represents a good compromise between accuracy of the calculations and computer time [13].

Then, we characterize the adsorption of atomic and molecular oxygen as well as ozone and water molecules at the divacancy sites. Note that the two lowest energy levels of atomic oxygen, i.e., $O(^3P)$ and $O(^1D)$ and, in a similar way, molecular oxygen both in its ground ($^3\Sigma g^-$) and excited ($^1\Delta g$) states are considered in our calculations.

The DFT calculations are based on the local spin density approximation (LSDA) [27] because this functional appears to be appropriate to study interactions on π-systems [28] and it is also known to often provide binding even for physisorbed molecules [29]. In a certain way, this prevents using more sophisticated methods taking into account weak interaction forces such as van der Waals corrected-DFT methods that have been recently used to study water physisorption on perfect graphene [30]. Moreover, because we consider adsorption on defective graphene surface, we expect chemical rather than physical interactions between the adsorbed molecules and the surface considered here.

Note that we use the quite modest 6-31G basis set because of the large number of atoms in the supercell. As a consequence of this reduced basis set, the comparisons between the different energy values given below should be considered in a relative way, only. All the calculations have been carried out by using the Gaussian 09 quantum chemistry package [31].

3. Results and discussion

The energy values associated with all the structures characterized in this work (using the DFT–LSDA/6-31G methodology) are given in Table 1 in atomic units (hartree) and all the energy values which appear in the following sections are thus deduced from the corresponding data. However, these values will be given in eV for convenience.

3.1. Optimized graphene structures containing one divacancy

Among the different configurations that can be optimized from a honeycomb lattice where two carbon atoms are removed, our calculations show the existence of three structures associated with three minima in the lowest potential energy surface (Fig. 1).

These three structures are characterized by a planar geometry and correspond to configurations where all dangling bonds are saturated at the vacancy site. The most stable divacancy structure is made of an arrangement of three pentagons and three heptagons instead of hexagons in perfect graphite (Fig. 1a). This vacancy is thus so-called a (555–777) defect. Another structure is also found in the optimization procedure, where an octagon is formed at the vacancy site with two neighboring pentagons. It is called the 5-8-5 defect, see Fig. 1b. The formation energy of this structure is found to be 0.84 eV higher than that of the 555–777 defect. In

Table 1
DFT–LSDA/6-31G energies of the structures involved in this study.

Structure	Energy (a.u.)
$O(^3P)$	−74.63979366
$O(^1D)$	−74.53536156
$O_2(^3\Sigma g^-)$	−149.52164103
$O_2(^1\Delta g)$	−149.46099689
$O_3(X^1A_1)$	−224.24096826
H_2O	−76.01518570
555–777 defect	−6062.31692524
5-8-5 defect	−6062.28593178
5-7-7-5 defect	−6062.18614565
Epoxy – 555–777 (Fig. 2a)	−6137.08960254
Ether – 5-8-5 (Fig. 2b)	−6137.19267599
Di-epoxy – 555–777 (Fig. 2c)	−6211.85693369
Epoxy – 555–777 – 2H (Fig. 2e)	−6138.26589535
Di-ether – 5-8-5 (Fig. 2d)	−6212.10379505
Ether – 5-8-5 – 2H (Fig. 2f)	−6138.29713149